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THE RELATIONSHIPS BETWEEN POLYMERS AND GLASS TRANSITION TEMPERATURES

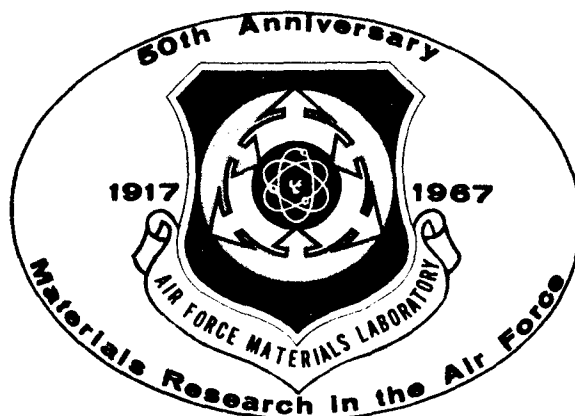
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THE RELATIONSHIPS BETWEEN POLYMERS AND

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L. V. Gallacher
American Cyanamid Company

September 1966

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FOREWORD

This report was prepared by the Central Research Division of American Cyanamid Company, Stamford, Connecticut, under USAF Contract No. AF 33(657)-11224. The contract was initiated under Project No. 7342, "Fundamental Research on Macromolecular Materials and Lubrication Phenomena", Task No. 734203, "Fundamental Principles Determining the Behavior of Macromolecules". It was administered under the direction of the Air Force Materials Laboratory, Research and Technology Division, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio with Dr. Ivan Goldfarb (MANP) as Project Engineer.

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This technical report has been reviewed and is approved.

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ABSTRACT

In recent years, it has been found that interdependence of the rotations of neighboring bonds is of primary importance to the physical behavior of polymers. Mathematical methods for handling interdependent rotations were developed by Lifson and others for the calculation of characteristic polymer dimensions. The Gibbs-DiMarzio theory of the glass transition in polymers is formulated in such a way that interdependent rotations may be taken into account. Using an empirically estimated value of 0.025 for the free volume fraction at the transition temperature, the Gibbs-DiMarzio theory was fitted to empirically estimated transition temperatures for the n-alkanes, hexane to eicosane. A good fit was obtained with $\epsilon_1 = 768$ cal/mole for the energy difference between trans and gauche states, and gauche rotations of opposite sign excluded.

The Adam-Gibbs theory of relaxation processes links the viscosity or relaxation time of a polymer to an energy barrier $\Delta\mu$, independent of temperature, and an independently rearranging region containing z^* segments, where z^* varies inversely with temperature. Values of z^* calculated from our viscosity data, assuming a minimum value of $k \ln 2$ for the configurational entropy of the critical region, were unreasonably small: one to four segments. A theory is presented by means of which z^* may be calculated from $(d \ln \tau / dP)_T$, avoiding the need for the $k \ln 2$ assumption. Using published data in addition to our own, the following values of $z^*(T_g)$ and $r^*(T_g)$, the radius of the critical region at the glass temperature, were found:

	<u>$z^*(T_g)$</u>	<u>$r^*(T_g)$</u>
Poly(propylene oxide)	220	11.6 Å
Poly(vinyl acetate)	341	17.0
Poly(vinyl chloride)	804	19.4

The average number of backbone bonds in a single chain through the critical region may be calculated from the above results. Chains were generated on a diamond lattice using a Monte Carlo technique, and the computed chain lengths for the three polymers ranged from 10 to 17. These are of the expected order of magnitude. Using these values of s in the cell theory developed earlier in this contract, along with viscosity-temperature data, the glass temperature may be accurately predicted.

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1. Glass Transitions in One-Dimensional Cooperative Systems

A. Introduction

The physical behavior of a liquid depends upon interactions between each molecule and its neighbors. As a first approximation, only nearest neighbors need be considered. Even so, the statistical treatment of such a three-dimensional cooperative system meets with serious difficulties. It would appear at first glance that the additional complications introduced by the long-chain nature of polymers would make the problem even more intractable. However, a polymer segment interacts much more strongly with the two neighbors to which it is bonded than with the others, so that it is possible to treat a polymer as a one-dimensional cooperative system with a relatively small correction for non-bonded neighbors.

Statistical methods of treating one-dimensional cooperative systems were first developed by Ising¹ and by Kramers and Wannier² in connection with the theory of ferromagnetism. Each unit is assumed capable of a discrete number of orientations whose energy depends on the orientation of its neighbors. Designating these orientations (or conformations) by ϕ^a, ϕ^b, \dots and assuming that all units have identical sets of conformations, then in the nearest-neighbor approximation, the energy of a chain of n units is given by

$$E(\phi_1, \phi_2, \dots, \phi_n) = \sum_{k=1}^n \epsilon(\phi_{k-1}, \phi_k) \quad (1)$$

where the summation is carried out over all pairs $(k-1, k)$ which are nearest neighbors and $\epsilon(\phi_{k-1}, \phi_k)$ are the interaction energies. The statistical weight matrix for each pair of units is a square array of order f , where f is the number of orientations available to each unit,

$$U = \begin{bmatrix} g(\phi^a, \phi^a) & \dots & g(\phi^a, \phi^f) \\ g(\phi^f, \phi^a) & \dots & g(\phi^f, \phi^f) \end{bmatrix} \quad (2)$$

and $g = \exp[-\epsilon(\phi_{k-1}, \phi_k)/kT]$. The partition function for such a system is given³ by

$$Q = 1/2 J^T U^n J \quad (3)$$

where J is the $f \times 1$ column matrix, each element of which is unity, and J^T is its transpose. In the polymer chain of n bonds to which Equation (3)

applies, the terminal bonds have equal energy in all rotational isomeric states and the second bond has a unique statistical weight matrix U_2 which must be determined individually. A symmetry number of $1/2$, not considered in Reference (3), has been included in Equation (3).

In the case of long chains, Equation (3) reduces to

$$Q = \lambda^n \quad (n \gg 1) \quad (4)$$

where λ is the largest eigenvalue of the matrix U^4 .

The physical properties of polymers in dilute solution are expected to conform with those of the model of a one-dimensional cooperative system described above. That is, interactions between polymer chains may be ignored provided the solution is sufficiently dilute. In good solvents, long-range interactions between polymer segments perturb the chain behavior, but at the Flory Θ point, interactions with solvent exactly compensate for long range segment interactions and the nearest-neighbor approximation is valid. Solvent effects on the unperturbed dimensions are small and may be taken into account by appropriate adjustments of the statistical weights in matrix U .

The physical properties of polymers in dilute solution which can be compared with the theory are the mean-square end-to-end length, dipole moment and optical anisotropy. The calculations involve matrices for the transformation of a vector in the coordinate system of bond k into that of bond $k-1$, as well as the statistical weight matrix U . Such calculations have been done for the one-dimensional cooperative model by Lifson,⁵ Gotlib,⁶ Hoeve,⁷ Nagai and Ishikawa,⁸ Birshtein and Ptitsyn⁴ and Flory and co-workers.³⁹ The agreement found with the experimental end-to-end length and its temperature coefficient and with experimental dipole moments demonstrates the applicability of the model to polymers in dilute solution. These results also demonstrate that neglect of correlations of orientations of neighboring units would invalidate the theory.

The temperature dependence of the end-to-end distance of polymer chains has immediate consequences to the theory of rubber elasticity.¹⁰ The theory of one-dimensional cooperative behavior is applied to undiluted networks of polymer chains by making the reasonable assumption that the change in equilibrium configurational entropy due to stretching is independent of the environment. Neighboring chains influence the configurational entropy and the rate of approach to equilibrium, but not the equilibrium difference in entropy between the stretched and unstretched states. The agreement between the predictions of this theory and experimental values of the retractive force as a function of temperature lends credence to the basic assumptions of rotational isomerism and one-dimensional cooperation.

The body of evidence described briefly above concerning the importance of intramolecular cooperative effects in polymer chains has been largely ignored in connection with the problem of the glassy state. This section is concerned with the incorporation of this feature into the Gibbs-DiMarzio theory of the glass transition.

B. Gibbs-DiMarzio Theory

The Gibbs-DiMarzio¹¹ treatment of the thermodynamic properties of amorphous polymers is based on a lattice model, similar to that of Flory¹² and Huggins.¹³ A system of N_x polymer chains of x units each is placed on a lattice of coordination number z in such a way that a fraction $V_0 = N_0/(N_0 + x N_x)$ of the lattice sites are vacant. Each backbone bond is capable of assuming f distinct orientations relative to the preceding bonds, the lattice of coordination number $f + 1$ being a sublattice of the other. The energy of each chain is a function of the relative orientations of the bonds, which can be expressed as in the nearest-neighbor approximation by Equation (1).

Certain sets of conformationally specified chains cannot be packed on a lattice in disordered array with reasonable values of V_0 . This gives rise to a negative configurational entropy at low temperatures, although the entropy has normal positive values at higher temperatures. A second-order transition occurs at the temperature T_2 at which the configurational entropy s_1 goes to zero. At higher temperatures the entropy is given¹¹ by

$$\frac{s_1}{R_x N_x} = \frac{z-2}{2} \ln \left(\frac{V_0}{S_0} \right) + \frac{V_0}{1-V_0} \ln (V_0^{z/2-1} / S_0^{z/2}) \\ + x^{-1} \ln \frac{[(z-2)x+2](z-1)}{2} + x^{-1} (\ln Q + T d \ln Q / dT), \quad (5)$$

where $S_0 = 1 - S_x$ and

$$S_x = \frac{[(z-2)x + 2]N_x}{[(z-2)x+2]N_x + zN_0}.$$

A significant feature of this treatment is that contributions arising from conformational properties of isolated chains appear as separate terms in the final equation, so that the partition function calculated for the one-dimensional chain can be used directly to calculate the configurational

entropy of a three-dimensional system. It follows from Equations (2), (3) and (5) that the glass temperature for a given pure homopolymer is determined by the appropriate values of z , V_0 , x and the statistical weight matrices U . The relation (5) is transcendental, but may be solved by iteration methods.

As a result of this separation of the inter- and intramolecular factors in the theory, quantitative applications to experimental data fall naturally into two classes: phenomenological relations between physical properties which are dependent only on z , V_0 and, through the relations given in References (11) and (14), on the intermolecular pair potential α and the volume of a lattice site $C(T)$; and relations between the transition temperature and the molecular properties x , n and U . As an example of the former, Voeks¹⁵ has used the theory to estimate the cohesive energy density and internal pressure of several polymers from density data alone, finding satisfactory agreement with experimental values.

Previous workers who have applied the theory to experimental transition temperatures have made the simplifying assumption that rotations of neighboring bonds are uncorrelated. Furthermore, the only case which has been considered is the chain in which all bonds have one conformer of low energy and two equivalent conformers higher in energy by some amount ϵ . Under these conditions Equation (3) reduces to¹¹

$$Q = 1/2 [1 + 2 \exp(-\epsilon/kT)]^{n-3}. \quad (6)$$

This form of the partition function is appropriate for a polymethylene chain, for example, and was used in the previous report¹⁶ for analysis of the data on n -alkanes. However, most polymers of interest exist as helices in the crystalline state, where any chain may form a helix of either screw sense. Hence, we expect that in general the chain bonds in most polymers will have at least two conformers of low energy, and Equation (6) does not apply. Furthermore, it has by now been abundantly demonstrated that correlations of rotations of adjacent bonds cannot be ignored in the case of chains bearing substituents on alternate chain atoms.

C. Empirical Estimation of Free Volume

In a commentary on the Gibbs-DiMarzio theory, Moacanin and Simha¹⁷ presented the following analysis of the factors which determine the transition temperature. The product $T_g(\alpha_L - \alpha_G)$ has been shown to be an almost universal constant for glass-forming materials, all the reported values falling in the range of 0.08 to 0.13, with a mean of 0.113.¹⁸ α_L and α_G are the expansivities of the liquid and glass, respectively. If it is assumed that the theoretical transition temperature T_2 is related to the experimental glass temperature by $T_2 \approx 0.8 T_g$, then $T_2(\alpha_L - \alpha_G) \approx 0.0904$. The Gibbs-DiMarzio expression for $T(\alpha_L - \alpha_G)$ is

$$T(\alpha_L - \alpha_G) = \frac{z\alpha V_0 S_x^2}{2kT} \left[\frac{zS_x}{2} - \frac{z\alpha S_0 S_x^2}{kT} - \left(\frac{z}{2} - 1 \right) \left(1 - V_0 \right) \right]^{-1} \quad (7)$$

For long chains this quantity is independent of x and only slightly dependent on z . The "universal" value of $T_2(\alpha_L - \alpha_G)$ corresponds to $V_0(T_2) \cong 0.025$.¹⁷ This coincides with the WLF value of the free volume at T_g , but refers of course to the free volume at the lower temperature T_2 .

The free volume is determined by the intermolecular pair potential α according to the following relationship^{11,14}

$$\ln (V_0^{z/2-1} / S_0^{z/2}) = z\alpha S_x^2 / 2kT. \quad (8)$$

For $V_0 = 0.025$ and $z = 4$, $\alpha/kT_2 = 1.30$.

If Equation (6) is used for the internal partition function, then it can be seen by inspection of Equations (5) and (6) that ϵ/kT is a function of V_0 and z only (for $x \rightarrow \infty$). For $V_0 = 0.025$ and $z = 4$, $\epsilon/kT_2 = 2.17$. The near coincidence of α/kT_2 and ϵ/kT_2 was observed by Eisenberg and Saito,¹⁹ who concluded that for all practical purposes the Gibbs-DiMarzio theory is a one-parameter theory. However, this result is a consequence of the use of Equation (6) for all polymers. The more general relations (2) and (3), with statistical weight matrices appropriate for each individual type of chain, would give rise to a wide spread in ϵ/kT_2 for different polymers, although α/kT_2 must still be close to the universal value of 1.30 (for $z = 4$ and $x \rightarrow \infty$).

D. Calculations for Polymethylene Chains

The free volume fraction $V_0(T_2)$ has been found empirically to be approximately 0.025 for a wide range of materials, as discussed above. This has the great pragmatic advantage of reducing the number of adjustable parameters in the comparison of Equation (5) with experimental data. In the last progress report¹⁶ the T_0 values for the n -alkanes were fitted to Equation (5) by using Equation (6) for the partition function (i.e., ignoring correlations of rotations). A method of estimating the intermolecular pair potential α was proposed and the free volume and flex energy were evaluated for selected values of z . The best fit was found to be $z = 6$, $V_0(T_0) = 0.04$ and $\epsilon = 340.0$ cal/mole.¹⁶ Since we now wish to allow for the correlations of rotations of neighboring bonds, and this will introduce one more parameter, the free volume fraction will be fixed at its universal value of 0.025 for the present purpose.

The T_0 values for n-alkanes were given in Reference (16). They represent the best value, obtained by a non-linear least-squares analysis, of this parameter in the equation

$$\log (\eta / d) = \log A + B / (T - T_0) . \quad (9)$$

The assumption is made that since $\log (\eta / d) \rightarrow \infty$ as $T \rightarrow T_0$, T_0 corresponds to the transition temperature T_2 . In order to compare $T_0(x)$ with the predictions of Equation (5), we must have the statistical weight matrix for the i th bond in the chain, where $i = 2, 3, \dots, n-2$. Bond 2 is assumed to have three conformers T, G and G' with statistical weights 1, σ and σ respectively, relative to the trans (T) conformation. Hence

$$U_2 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \sigma & 0 \\ 0 & 0 & \sigma \end{bmatrix} \quad (10)$$

where $\sigma = \exp (-\epsilon_1 / kT)$. Subsequent bonds encounter a situation of much higher energy whenever gauche rotations of opposite sign occur in pairs. This is the well-known pentane effect¹⁹ and results in an additional factor $\omega = \exp (-\epsilon_2 / kT)$ in the statistical weight, which is so small as to virtually exclude such states. Hence for all subsequent bonds i where $i = 3, 4, \dots, n-2$ the statistical weight matrix has the form

$$U = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & \sigma\omega \\ 1 & \sigma\omega & \sigma \end{bmatrix} \quad (11)$$

The partition function may be evaluated by the use of Equation (3) and substituted in Equation (5). For a constant free volume fraction at T_2 this takes the form

$$\begin{aligned}
0 = & \frac{z-2}{2} \ln \left[1 - \frac{2(1-v_0)}{z} + \frac{2(1-v_0)}{zx} \right] \\
& + \frac{v_0}{1-v_0} \ln \left\{ \left[1 - \frac{2(1-v_0)}{z} + \frac{2(1-v_0)}{zx} \right]^{z/2} v_0^{-1} \right\} \\
& + x^{-1} \ln \left\{ [(z-2)x+2](z-1)/2 \right\} + x^{-1} [\ln Q + T_2(d \ln Q/dT)_{T_2}] \quad (12)
\end{aligned}$$

Assuming that each methylene group occupies one lattice site, then x is simply the number of carbon atoms in the chain.

In calculating the partition function for a polymethylene chain, it is possible to take advantage of the symmetric properties of the coefficient matrix U_2^{n-3} and obtain a relatively simple explicit formula. It can be derived in the following manner.

$$\text{Let } U_2^{1/2} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \sqrt{\sigma} & 0 \\ 0 & 0 & \sqrt{\sigma} \end{bmatrix} \text{ and } A = \begin{bmatrix} 1 & 1 & 1 \\ 1 & 1 & \omega \\ 1 & \omega & 1 \end{bmatrix}$$

Then since

$$U = AU_2, \quad (13)$$

we may write

$$Q = J^T U_2^{1/2} (U_2^{1/2} A U_2^{1/2})^{n-3} U_2^{1/2} J. \quad (14)$$

Since $U_2^{1/2} A U_2^{1/2}$ is symmetric

$$H^T (U_2^{1/2} A U_2^{1/2}) H = \Lambda \quad (15)$$

where Λ is the diagonal matrix of eigenvalues of $U_2^{1/2} A U_2^{1/2}$ and the columns of H are the corresponding normalized eigenvectors. Hence

$$Q = J^T U_2^{1/2} (H \wedge H^T)^{n-3} U_2^{1/2} J, \quad (16)$$

$$= J^T U_2^{1/2} H \wedge^{n-3} H^T U_2^{1/2} J, \quad (17)$$

$$= \underline{L}^T \wedge^{n-3} \underline{L} = \sum_{i=1}^3 \ell_i^2 \lambda_i^{n-3} \quad (18)$$

where $\underline{L} = H^T U_2^{1/2} J$. The eigenvalues of $U_2^{1/2} A U_2^{1/2}$ are

$$\lambda_1 = \sigma(1 - \omega) \quad (19)$$

$$2\lambda_2 = 1 + \sigma(1 + \omega) + [\sigma^2(1 + \omega)^2 + 2\sigma(3 - \omega) + 1]^{1/2} \quad (20)$$

$$2\lambda_3 = 1 + \sigma(1 + \omega) - [\sigma^2(1 + \omega)^2 + 2\sigma(3 - \omega) + 1]^{1/2} \quad (21)$$

and if we let

$$c_1 = [\sigma^2(1 + \omega)^2 + 2\sigma(3 - \omega) + 1]^{1/2} \quad (22)$$

$$c_2^2 = 16\sigma + 2[1 - \sigma(1 + \omega) - c_1]^2 \quad (23)$$

$$c_3^2 = 16\sigma + 2[1 - \sigma(1 + \omega) + c_1]^2 \quad (24)$$

then the eigenvector matrix is given by

$$H = \begin{bmatrix} 0 & -4\sigma^{1/2}/c_2 & -4\sigma^{1/2}/c_3 \\ -2^{-1/2} & [1 - \sigma(1 + \omega) - c_1]/c_2 & [1 - \sigma(1 + \omega) + c_1]/c_3 \\ 2^{-1/2} & [1 - \sigma(1 + \omega) - c_1]/c_2 & [1 - \sigma(1 + \omega) + c_1]/c_3 \end{bmatrix} \quad (25)$$

It thus follows that $l_1 = 0$ and

$$Q = l_2^2 \lambda_2^{n-3} + l_3^2 \lambda_3^{n-3} \quad (26)$$

$$= 16 \sigma \left\{ \frac{\lambda_2^{n-1}}{c_2^2} + \frac{\lambda_3^{n-1}}{c_3^2} \right\}. \quad (27)$$

With this substitution in Equation (12), and remembering that $\sigma = \exp(-\epsilon_1/RT_2)$ and $W = \exp(-\epsilon_2/RT_2)$, the transition temperature $T_2(n)$ may be calculated for given values of ϵ_1 , ϵ_2 , z and V_0 . A program was written by the Mathematical Analysis Section for fitting Equation (12) to the $T_0(n)$ values for the n -alkanes by adjusting ϵ_1 and ϵ_2 , taking $V_0 = 0.025$ and various integral values of z . The best least-squares fit was obtained for $z = 4$, $\epsilon_1 = 768$ cal/mole and $\epsilon_2 = \infty$. The predicted transition temperatures are compared with the observed $T_0(n)$ values in Table I.

It was found that the function $T_2(n)$ drops too sharply for small n to fit the T_0 values for $n < 5$, so these values were excluded from the least-squares analysis. This behavior probably results from the assumption of a constant V_0 , which may not be realistic for short chains.

The best-fit values of ϵ_1 and ϵ_2 are in excellent accord with the values 800 and ∞ , respectively, found by Nagai and Ishikawa⁸ for polyethylene. However, later analyses by Hoeve,⁷ and Abe, Jernigan and Flory³ resulted in the somewhat lower values $\epsilon_1 = 500$ and $\epsilon_2 = 1800$ cal/mole. Nevertheless, the agreement is considered good enough to substantiate the basic assumptions of the theory of the one-dimensional cooperative model.

TABLE I

Predicted Transition Temperatures for n-Alkanes

Parameters: $z = 4$, $V_0 = 0.025$, $\epsilon_1 = 768$ cal/mole, $\epsilon_2 = \infty$.

<u>Chain Length</u> <u>$n = x-1$</u>	<u>Calculated</u> <u>T_2 ($^{\circ}\text{K}$)</u>	<u>Observed</u> <u>T_0 ($^{\circ}\text{K}$)</u>	<u>Difference</u>
5	86.842	97.581	10.739
6	103.073	104.91	1.837
7	113.153	113.29	0.137
8	120.480	119.40	-1.080
9	126.215	124.76	-1.455
10	130.907	129.27	-1.637
11	134.861	132.51	-2.351
12	138.266	135.76	-2.506
13	141.245	138.37	-2.875
14	143.887	142.00	-1.887
15	146.253	144.49	-1.763
16	148.391	148.30	-0.091
17	150.336	150.80	0.464
18	152.116	154.99	2.874
19	153.755	157.07	3.315

2. Evaluation of the Adam-Gibbs Theory with Polymer Melt Viscosities

A. Introduction

During the last phase of this contract¹⁶, viscosity measurements were made on a number of low molecular weight polymers at temperatures between 25°C and 90°C. The purpose of this work was to amass polymer viscosity data over a broad enough range of molecular weights and temperatures so that current theories of molecular motion in polymers could be evaluated. In this report, we will discuss the Adam-Gibbs theory²⁰ of relaxation in glass-forming liquids.

B. Estimation of the Segmental Free-Energy Barrier

In a recent paper,²⁰ Adam and Gibbs described a theory for cooperative relaxation processes in glass forming liquids, with emphasis on polymer behavior. An equation was derived linking the relaxation time or viscosity to a free energy barrier:

$$\log \eta = A' + \frac{s_c^* \Delta \mu}{2.303 k \Delta C_p T \ln T/T_2} . \quad (28)$$

Here s_c^* is the minimum configurational entropy of the critical region involved in the relaxation process, $\Delta \mu$ is the free energy barrier per mole of backbone atoms, ΔC_p is the change in specific heat in passing through the glass transition, and T_2 is the equilibrium second-order transition temperature.¹⁴ A' is a term which, according to transition state theory,²² is proportional to the reciprocal of the volume of a moving segment. Thus, it is more reasonable to use the kinematic viscosity, ν , in Equation (28).²³ The critical configuration entropy, s_c^* , will have a minimum value of $k \ln 2$, assuming that there must be a minimum of two configurations available to the critical region. It is conceivable that s_c^* might be greater than two in some cases. In this discussion, however, we will assume that $s_c^* = k \ln 2$. Substitution into and simplification of Equation (28) now yields

$$\log \nu = A + \frac{B}{T \ln T/T_2} , \quad (29)$$

where

$$B = \frac{s_c^* \Delta \mu}{2.303 k \Delta C_p} = 0.301 \frac{\Delta \mu}{\Delta C_p} . \quad (30)$$

During the last phase of the contract,¹⁶ the best-fit values of A, B, and T_2 were evaluated for polypropylene, poly(propylene oxide) (PPG), and poly(chlorotrifluoroethylene) (PCFE). These are given in Table II. With these parameters, a value for s_c^* , and knowledge of ΔC_p , it should be possible to estimate $\Delta\mu$. With this in mind, we set out to analyze the least-squares results obtained for Equation (29) with our polymers.

Values for ΔC_p are available for a relatively small number of polymers. Therefore, it was necessary in some cases to utilize the "universal" value of ΔC_p of 2.7 calories per mole of chain atoms per degree suggested by Wunderlich.²⁴

In addition to our own data, we analyzed some results for polyisobutylene and polystyrene published by Fox and Flory.²⁵ Values of B were taken from results computed previously for the Fulcher Equation,^{16,31}

$$\log \eta = A + \frac{B}{T - T_0}, \quad (31)$$

when it was observed that the difference in B as determined with Equations (29) and (31) was less than ten per cent. Thus, the error in $\Delta\mu$ calculated with Equation (31) will be relatively small. These B values are given in Table II. Table III is a compilation of the results. We have included in the table a listing of cohesive energy densities, calculated according to Small's³⁶ method, and a listing of glass transition temperatures.

Examination of Table III shows that $\Delta\mu$ varies in about the way one would anticipate, based on molecular structure considerations. Polyisobutylene has the largest value as one might expect from its tight structure. Poly(propylene oxide) has the smallest value for $\Delta\mu$. The ether linkage makes a large contribution to backbone flexibility in this polymer. The fact that the smaller values of $\Delta\mu$ lie around 3 kcal per mole is an indication that the barriers to internal rotation around backbone C-C bonds may be more important than interactions between non-bonded neighboring groups in determining transport properties for some polymers, but in general the non-bonded interactions are significant.

C. The Size of the Critical Region at T_g

We have reported in the past^{16,27} that activation free energies for a number of polymers have values near 25 kcal per mole at the glass temperature. Based on the $\Delta\mu$ values we obtained, this suggests that the size of the cooperative region involved in viscous flow may be quite small. A full treatment follows. In the Adam-Gibbs derivation, the free energy of activation ΔG^\ddagger is given as $z^* \Delta\mu$, where z^* is the number of monomer units contained in the smallest region capable of rearranging.

TABLE II

The Best-Fit Parameters in the Adam-Gibbs Equation

<u>Polymer</u>	<u>$M_n \times 10^{-4}$</u>	<u>A</u>	<u>B</u>	<u>T_2</u>
Polypropylene	0.090	-1.182	841	171.6
	0.121	-1.220	974	172.4
Poly(propylene oxide)	0.046	-0.786	392	180.7
	0.125	-0.336	403	177.0
	0.208	-0.070	409	175.3
	0.362	0.036	619	148.7
Poly(chlorotrifluoroethylene)	0.064	-0.982	338	164.8
	0.082	-1.223	521	186.5
	0.105	-1.811	938	166.0
Polyisobutylene	0.076*	-	1064	-
	0.54*	-	1242	-
	1.29*	-	1318	-
Polystyrene	0.359*	-	645	-
	0.665*	-	624	-
	1.330*	-	654	-

* Viscosity-average molecular weight.

TABLE III

Values of $\Delta\mu$ Computed with Equation 3

Polymer	$\bar{M}_n \times 10^{-4}$	ΔC_p , cal/mole deg.	$\Delta\mu$ kcal	CED	Tg, °C
<u>Polypropylene</u>					
C-60	0.090	2.3 ^a	6.4	62	-50
C-175	0.121	2.3 ^a	7.4	62	-35
<u>Poly(propylene oxide)</u>					
P-400	0.046	2.7 ^b	3.5	59	-69
P-1200	0.125	2.7 ^b	3.6	59	-67
P-2000	0.208	2.7 ^b	3.7	59	-67
P-4000	0.362	2.7 ^b	5.6	59	-66
<u>Poly(chlorotrifluoroethylene)</u>					
FS-5	0.064	2.7 ^b	3.0	62	-
S-30	0.082	2.7 ^b	4.7	62	-
LG-160	0.105	2.7 ^b	8.4	62	-50
<u>Polyisobutylene^c</u>					
	0.076 ^g	2.67 ^d	9.4	60	-
	0.54 ^g	2.67 ^d	11.0	60	-76 ^e
	1.29 ^g	2.67 ^d	11.7	60	-68 ^e
<u>Polystyrene^c</u>					
	0.359 ^g	3.5 ^f	7.5	75	75
	0.665 ^g	3.5 ^f	7.3	75	77
	1.330 ^g	3.5 ^f	7.6	75	86

^a Taken from T. P. Melia, J. Appl. Chem., 14, 461 (1964).^b Based on the universal value observed by B. Wunderlich. See Ref. (24).^c All polyisobutylene and polystyrene viscosity data are taken from T. G. Fox, Jr., and P. J. Flory, J. Appl. Phys., 21, 581 (1950); and T. G. Fox, Jr., and P. J. Flory, J. Phys. Chem., 55, 221 (1951). Corrections for the polystyrene molecular weights were published later in T. G. Fox and P. J. Flory, J. Polymer Sci., 14, 315 (1954).^d See Ref. (24), B. Wunderlich.^e Polyisobutylene glass temperatures were based on the relationship proposed by Fox and Flory in 1950: $T_g, ^\circ\text{C} = -63 - 6.9 \times 10^4/M$. See T. G. Fox, Jr., and P. J. Flory, J. Appl. Phys., 21, 581 (1950). The value they propose for $T_{g\infty}$, -63°C , is several degrees higher than the accepted value, but agrees well with differential thermal analysis values obtained in these laboratories.^f Taken from F. E. Karasz, H. E. Bair, and J. M. O'Reilly, J. Phys. Chem., 69, 2657 (1965).^g Viscosity average molecular weights of fractions.

They recognized that ΔG^\ddagger is temperature dependent. This temperature dependence is totally contained in z^* , and it is assumed that $\Delta\mu$ does not vary. The assumption of a temperature independent $\Delta\mu$ is not especially appealing, since it seems reasonable to expect non-bonded interactions to be quite temperature sensitive. However, if one assumes that rotational barriers constitute most of $\Delta\mu$, then the temperature independence is more reasonable. The results given in Table III indicate that the situation varies considerably from polymer to polymer, but we will continue our development assuming fixed $\Delta\mu$ values. The free-energy of activation can be obtained from the terms in Equation (29) using the identity

$$\frac{\Delta G^\ddagger}{2.303 RT} = \frac{B}{T \ln T/T_2}, \quad (32)$$

which leads to

$$\Delta G^\ddagger = \frac{RB}{\log T - \log T_2} \quad (33)$$

Now, combining Equations (30) and (33) we obtain

$$z^* = \frac{0.60}{(\log T - \log T_2)\Delta C_p} \quad (34)$$

Thus, the size of the cooperative region is a function only of ΔC_p and the ratio T/T_2 . Of course, we assumed here, as before, that sc^* is equal to $k \ln 2$, i.e., that the critical region is capable of rearranging to only one other configuration. Values of z^* at the glass temperature have been determined with Equation (34) and are given in Table IV.

It is apparent that the values of z^* are too small to be in agreement with reality. This may be the result of underestimating the configurational entropy of the critical region. If we assume that z^* is in error by some fixed factor, then it still is possible to obtain a meaningful interpretation of the data.

Since z^* probably reflects intermolecular barriers (due to long range non-bonded interactions) more than rotational barriers, it seems reasonable to expect large values of z^* at the glass temperature (z_g^*) in polymers where the transition is primarily the result of large intermolecular potential energy barriers. The intermolecular barrier exists because rotation around chain bonds requires sweeping through relatively large volumes of space. This rotation by itself would require a tremendous amount

TABLE IV

The Size of the Critical Region at T_g Based on $s_c^* = k \ln 2$

Polymer	$M_n \times 10^{-4}$	C_p , cal/mole	$\log T_g/T_2$	z^* , Chain Atoms
Polypropylene	0.090	2.3	0.113	2.31
	0.121		0.141	1.85
Poly(propylene oxide)	0.046	2.7	0.052	4.27
	0.125		0.065	3.42
	0.208		0.070	3.17
	0.362		0.144	1.54
Poly(chlorotrifluoroethylene)	0.105	2.7	0.128	1.74
Polyisobutylene	0.54*	2.67	0.200	1.12
	1.29*		0.248	0.91
Polystyrene	0.359*	3.5	0.060	2.85
	0.665*		0.047	3.64
	1.330*		0.054	3.17

* Viscosity average molecular weights.

of energy because of non-bonded interactions. However, it seems likely that simultaneous motions in the vicinity of the rotation reduce the barrier height considerably.

What gives rise to large intermolecular barriers? In general, it must be any factor which would increase the long-range non-bonded interactions, e.g., bulky, rigid side groups; strong dipoles; hydrogen bonding capacity; ionic and ion-dipole-interactions; and close packing.

In polymers with large rotational barriers, it seems likely that backbone relaxation times will approach the T_g range ($\sim 10^3$ seconds) before the intermolecular barrier has grown very large. Therefore, z^* will remain small. Polymers with small rotational barriers and no large pendant groups, like polypropylene oxide, are influenced largely by packing (and hydrogen bonding to some extent), which leads to a low glass temperature and a large z^* value.

Further consideration of Equation (34) is in order. If we assume that ΔC_p is at or near its most likely value of $2.7 \text{ cal deg}^{-1} \text{ mole}^{-1}$, then z^* is a function of T/T_2 only. A small value for T/T_2 leads to a large value for z^* and vice versa. In order to agree with the present argument, a small T/T_2 ratio corresponds to a large intermolecular barrier and a large T/T_2 ratio corresponds to a relatively large rotational barrier. This is exactly what one would predict, since the intermolecular barrier will increase sharply with decreasing temperature in the neighborhood of T_g , while the rotational barrier will be insensitive to temperature. Thus, the greater the influence of the rotational barrier, the more closely the polymer will conform to Arrhenius behavior.

D. An Alternate Approach to z^* Based on Transition State Theory

Unreasonably small values of z^* and large values of $\Delta\mu$ result when the $k \ln 2$ approximation for the configurational entropy of the critical region is used in the calculations. This makes it rather difficult to obtain the maximum benefit from the Adam-Gibbs theory, for it is far from clear what value of s_c^* would be appropriate. There is, however, at least one other way of estimating the size of the critical region z^* , and this will be discussed here.

If we start with the assumption that the critical region is spherical, it can be seen that the radius of this region in angstroms is given by

$$r = \left[\frac{3 z^* V_b (10^{24})}{4\pi N} \right]^{1/3} \quad (35)$$

where V_b is the molar volume per backbone atom in cc, z^* is the number of backbone atoms in the region, and N is Avogadro's number.

We wish to obtain the volume of the critical region at the glass temperature. In order to do this we must first determine the value of z^* at the glass temperature.

In 1957 Gee²⁸ suggested that the activation process in the flow of liquids involves an expansion equal to Δv^+ , the volume of activation, in the neighborhood of the molecule which is going to move. In order to relate Δv^+ to the cooperative region, it is reasonable to use the approach of Cohen and Turnbull.²⁹ They proposed that redistribution of the free volume in the cooperative region leads to local hole formation, which in turn permits motion. Thus, the critical or cooperative region is essentially a region with close to the macroscopic density, but with enough free volume so that a density fluctuation within the region can give rise to an activated site. If, as Adam and Gibbs²⁰ suggest, the cooperative region is the smallest one that can rearrange, then it follows that Δv^+ must be very close to the total free volume of the critical region. This means that

$$\Delta v^+ = v z^* , \quad (36)$$

where v is the free volume per backbone atom (on a molar basis). Now we define the free volume fraction f as v/V_b and obtain the following for z^* :

$$z^* = \frac{\Delta v^+}{f V_b} . \quad (37)$$

Accepting the WLF³⁰ free volume definition, we have $2.303 c_1^g$ in place of f at the glass temperature. In terms of the Fulcher³¹ equation parameters, f is given by $(T-T_0)/2.303 B$, where B and T_0 are adjustable parameters. Both free volume fractions are identical at T_g . In our case, since we have determined the Fulcher parameters for the polymers of interest, we will use the form

$$z^* = \frac{2.303 \Delta v^+ B}{V_b (T-T_0)} \quad (38)$$

with T equal to T_g .

It remains now to evaluate Δv^\ddagger . Since the pressure dependence of the Gibbs free energy at constant temperature is simply the volume, it follows from transition state theory that

$$\left(\frac{\partial \ln \tau}{\partial p} \right)_T = - \frac{\Delta v^\ddagger}{RT} \quad (39)$$

Here τ is the average relaxation time for the principal (α) process in the system. We make the assumption that τ is independent, or nearly so, of the type of measurement.¹⁶ What is necessary, then, is the variation of τ with pressure at constant temperature. Using the $(\partial \log \tau / \partial p)_T$ results of Williams³² for PPG and of O'Reilly³³ for PVAc and PVC, we have determined Δv^\ddagger at several temperatures for each polymer and then extrapolated to the glass temperature. V_b is evaluated at the glass temperature using the expansion coefficient and specific volume measured at higher temperatures.

Finally z^* is calculated using Equation (38). The values of z^* at T_g are presented in Table V along with Δv^\ddagger , V_b , and f measured at or extrapolated to the glass temperature.

TABLE V

The Size of the Critical Region and
Associated Parameters at the Glass Temperature

Polymer	z^*	Δv^\ddagger , cc/mole	V_b , cc/mole	f
Poly(propylene oxide)	220	140	17.7	0.036
Poly(vinyl acetate)	341	265	36.1	0.025
Poly(vinyl chloride)	804	460	22.9	0.025

It is apparent that the values of z^* at T_g are much larger here than those obtained using the Adam-Gibbs theory with the $k \ln 2$ approximation for the configurational entropy of the critical region. Therefore, it appears that the entropy is much greater than the minimum value assumed previously.

Proceeding to the calculation of the radius of the critical region using Equation (35), we find that r equals 11.6, 17.0, and 19.4 angstroms for poly(propylene oxide), PVAc, and PVC taken in the same order.

E. The Size of a Relaxing Chain Segment

We now proceed to an important aspect of the problem--the computation of the average number of backbone bonds in a single continuous chain in the critical region. This quantity should be a measure of the maximum number of backbone bonds in a continuous polymer chain perturbed by rotation about a single backbone bond within the chain. We will assume that the chains are of infinite molecular weight, thus eliminating chain ends, and possess their unperturbed dimensions. Consider a sphere of volume equal to that of the critical region. Each chain which passes through the sphere is cut by the surface at two points. The problem is to determine the average number of backbone bonds for any single chain between the point of entry and the first point of departure from the sphere.

Although an analytical solution to this sort of problem may exist for long chains with free rotation, the complexity added by short chains and rotational angle correlations makes a solution very difficult to obtain. On the other hand, the problem can be handled easily for short chains with any desired rotational correlations using Monte Carlo techniques. Therefore, we selected the latter approach.

The necessary computations were performed on an SDS 925 digital computer using a Fortran II program. In order to obtain the desired result, it was necessary to formulate a correct model. The important features of the final model are explained below:

(1) Chain Generation. If one starts with a central point representing a tetrahedral carbon atom, it is possible to generate eight "bonds" emanating from it, which determine two mutually exclusive tetrahedral lattices. The x, y, and z components of each bond vector are assigned values of + 1, giving a bond length of $\sqrt{3}$. It is easily shown that the four bonds in the first lattice are $\bar{1}11$ ($x = -1, y = 1, z = 1$), $1\bar{1}1$, $11\bar{1}$, and 111 . The four bonds in the second lattice are $11\bar{1}$, $\bar{1}1\bar{1}$, $1\bar{1}\bar{1}$, and $\bar{1}\bar{1}\bar{1}$. For each of these initial bonds or steps, the next step is obtained by changing the sign of one of the components. Thus, for each step, there are three possible second steps. One of the three is selected on the basis of a random number generated by the computer program. Succeeding steps are taken in the same way.

This program starts by generating a point randomly on the surface of the sphere. Then an attempt is made to generate eight random walks through the sphere, each walk initiated by one of the eight first steps. Each of the four successful walks is continued until it again passes through the surface of the sphere. The points of entry and exit and the total number of steps, including fractions, are recorded and stored for further computations.

(2) Entry of a Chain into the Sphere. For situations where the bond length is within approximately two orders of magnitude of the radius, it is essential that the direction of the first chain bond entering the sphere be selected randomly. In three dimensions, this required that the angle θ between the bond and the surface at the point of entry have a probability density proportional to $\cos \theta$. There are several approaches to this problem. The one used was to place the starting point of the chain randomly on the surface of the sphere without changing the eight initial step vectors. In order to generate a point on the surface, we first generated a point randomly inside the sphere and then projected it to the surface.

(3) Internal Rotational Angles. One of the advantages of the tetrahedral lattice is its equivalence to the rotational isomeric model with allowed rotational angles of 0° , 120° , and 240° (measured from the trans portion). This makes it possible to incorporate any desired correlations among rotational angles into the computation at the expense of computer time only.

The simplest approximation is to assign statistical weights to trans and gauche sequences based on experimental determinations of the flex energy, i.e., the energy difference between trans and gauche states. Results obtained from the measurement of stress-temperature coefficients of cross-linked networks and from the temperature dependence of the intrinsic viscosity of unperturbed polymers indicate that real chains can be represented quite well in most cases with flex energies in the range of 300 to 500 calories per mole. Therefore, we used both 300 and 500 calories as flex energies in the computations and 300°K as the temperature.

In performing the computations, it was assumed that all bonds in the chains were of equal length. This is a reasonable assumption for the polypropylene oxide chains as well as the carbon backbone chains, since the C-O bond is only 0.03 angstroms shorter than the C-C bond. Since flex energies of 300 and 500 cal/mole gave chains with nearly identical configurational properties, we present only the results for 500 cal/mole in Table VI.

TABLE VI

Results of Monte Carlo Simulation of Chains
in Cooperative Region at T_g

<u>Polymer</u>	<u>Volume, \AA^3 $z^* V_b$</u>	<u>Radius, \AA</u>	<u>Average Number of Bonds</u>	<u>Mean Square End-to-End Distance, \AA^2</u>
PPG	3,890	11.6	9.8	48
PVAc	12,300	17.0	15.	75
PVC	18,400	19.4	17.	86

It is interesting to find that the number of bonds in a single chain contained in the critical region is on the order of 10.

F. Cell Model for the Glass Transition

The results described in the preceding section agree surprisingly well with the cell theory developed earlier in this contract,²⁷ which gives good predictions of the glass temperature with chain segments of 5 or 10 atoms. As a test of the results, we used the cell theory to predict T_g values for each of the poly(propylene oxide) polymers studied. The theory was applied using the best fit values of A, B, and T_0 in the viscosity equation

$$\log \eta = A + \log \rho + \frac{B}{T - T_0}, \quad (40)$$

where ρ is the polymer density in g/cc. The equation for the cell model was rearranged to the form

$$T_g = T_0 + \frac{B}{\frac{2}{3} \log \frac{4\pi N \rho}{3s} - \frac{5}{3} \log M' + \log \frac{tR \langle h^2 \rangle_0 / M}{6} T_g M^* - A}, \quad (41)$$

where

- N = Avogadro's number,
- s = 10, the average number of bonds in a single continuous chain in the critical region,
- M^* = the effective weight-average molecular weight,
- M' = the molecular weight per backbone atom,
- t = the characteristic time for T_g , taken as 10^3 seconds,
- R = the gas constant, 8.31×10^7 ergs/mole deg.,
- $\langle h^2 \rangle_0 / M$ = the ratio of the unperturbed mean square end-to-end distance to the molecular weight, a quantity tabulated in the literature for many polymers.³⁴

The effective molecular weight M^* depends on the existence of chain entanglements in the melt. Below a molecular weight M_c , the melt viscosity is linear in the first power of the weight average molecular weight. In the region above M_c , the viscosity is linear in the molecular

weight to the 3.4 power. This phenomenon has been attributed by Bueche³⁵ to the formation of chain entanglements. The effect of entanglements is to increase the effective molecular weight by forcing entangled molecules to act as single large molecules. Thus, above M_c the effective molecular weight is linear in the actual molecular weight to the 3.4 power. Below M_c the value of M^* is conveniently equal to M .

In considering equations of the same sort as Equation (40), Fox,³⁶ Bueche,³⁷ and others have observed that the molecular weight dependence of the melt viscosity is contained entirely in the parameter A as long as the molecular weight has reached a large value, in the neighborhood of 10^5 . This means, of course, that A and $\log M^*$ are directly proportional and therefore the denominator in Equation (41) is essentially independent of the molecular weight. It has been observed by us and others that B and T_0 are also independent of molecular weight at sufficiently high molecular weights. Thus, T_g itself will be independent of the molecular weight in high molecular weight polymers. This is in complete accord with experimental results.

Commercial low-molecular-weight poly(propylene oxides) are known to have very narrow molecular weight distributions, with M_w/M_n less than 1.10. Therefore, the number average molecular weights were used in the cell model calculations.

The predicted and experimental T_g values are tabulated below.

TABLE VII

Predicted Values of T_g of Poly(propylene oxides),
Based on Cell Model

<u>Molecular Weight (M_n)</u>	<u>Glass Temperature, °K</u>	
	<u>Predicted</u>	<u>Experimental (DTA)</u>
460	210	204
1250	207	206
2080	206	206
3620	192	207

In general, there is excellent agreement between prediction and experiment. However, in the case of the highest molecular weight polymer, the prediction is 15 degrees in error. This may be the result of a rather poor fit of Equation (40) to the viscosity data for this polymer.¹⁶

As a result of this study, we conclude that the Adam-Gibbs theory is a very logical approach to the problem of motion in glass-forming liquids. It includes at once the concept of an equilibrium second-order transition temperature and the experimentally observed effects of time-dependent phenomena on the transition. Unfortunately, however, it is not a simple matter to obtain quantitative information from the theory, since this hinges on the estimation of the configurational entropy of the critical region.

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13. ABSTRACT The Gibbs-DiMarzio theory of the glass transition in polymers is formulated in such a way that interdependent rotations may be taken into account. Using an empirically estimated value of 0.025 for the free volume fraction at the transition temperature, the Gibbs-DiMarzio theory was fitted to empirically estimated transition temperatures for the <u>n</u> -alkanes, hexane to eicosane. A good fit was obtained with $\epsilon_1=768$ cal/mole for the energy difference between trans and gauche states, and gauche rotations of opposite sign excluded. The Adam-Gibbs theory of relaxation processes links the viscosity or relaxation time of a polymer to an energy barrier $\Delta\mu$, independent of temperature, and an independently rearranging region containing z^* segments, where z^* varies inversely with temperature. Values of z^* calculated from our viscosity data, assuming a minimum value of $k \ln 2$ for the configurational entropy of the critical region, were unreasonably small: one to four segments. A theory is presented by means of which z^* may be calculated from $(d \ln \bar{T}/dT)_T$, avoiding the need for the $k \ln 2$ assumption. The average number of backbone bonds in a single chain through the critical region may be calculated. Chains were generated on a diamond lattice using a Monte Carlo technique, and the computed chain lengths for the three polymers ranged from 10 to 17. These are of the expected order of magnitude. Using these values of s in the cell theory developed earlier in this contract, along with viscosity-temperature data, the glass temperature may be accurately predicted.			

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